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ANALYSIS OF BRUCE NGS "A" UNIT 3 STEAM GENERATOR 3 DEPOSITS

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Report No 86-82-K

ABSTRACT

A tube and adjacent deposits from the tubesheet region of Bruce NGS "A", Unit 3, Steam Generator 3 were analyzed. The results showed that the composition of free tube deposits sampled near the tubesheet was similar to that of the free surface deposits which had been previously obtained from the U-bend region in other steam generators at Bruce NGS "A". The deposits in the tubesheet rolled joint crevice were likely to be the result of particulate deposition and/or hideout precipitation and not locally grown magnetite from corrosion of the tube-sheet carbon steel. Sludge pile deposits may have contained important concentrations of relatively soluble species such as alkaline and alkaline-earth metal silicates, sulphates and chlorides. These species may not be necessarily detrimental to the materials integrity as long as the oxidation potential of the system is low. However, a shift in this potential induced by a change in pH and/or the presence of oxidizing species may cause unacceptable material corrosion. The removal of the sludge pile would minimize the impact of such an event.

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EXECUTIVE SUMMARY

ANALYSIS OF BRUCE NGS "A" UNIT 3 STEAM GENERATOR 3 DEPOSITS

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A tube section and adjacent tube deposits from the tubesheet region of Bruce NGS "A", Unit 3, Steam Generator 3 were analyzed using several analytic techniques. Some deposits remained on the tube surface after sampling and originated from free surfaces, the rolled joint tubesheet crevice and the region under the sludge pile. Other deposits were directly sampled from the sludge pile.

The composition of the free surface deposits, mainly magnetite and metallic copper, was similar to that of free tube deposits previously obtained from the U-bend region in other steam generators at Bruce. The deposits in the tubesheet rolled joint crevice are likely to be the result of particulate deposition and/or hideout precipitation and not locally grown magnetite from corrosion of tubesheet carbon steel. The height of the sludge pile near the tube was approximately 20 mm. This was in agreement with field measurements. The sludge pile deposits may have contained important concentrations of species such as alkaline and alkaline-earth metal silicates, sulphates and chlorides while the remainder consisted of magnetite, metallic copper and cuprite (cuprous oxide). Chemical analysis results and the probable physical characteristics of the sludge pile indicated that high concentrations of sodium and potassium chlorides may exist under the pile during operation and shutdown. These high contaminant concentrations may not be necessarily detrimental to the materials integrity as long as the oxidation potential of the system is low. However, a shift in this potential induced by a change in pH and/or the presence of oxidizing species may cause unacceptable material corrosion. The removal of the sludge pile would minimize the impact of such an event.

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To: Mr. B. Montford
Manager - Chemistry & Metallurgy
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ANALYSIS OF BRUCE NGS UNIT 3
STEAM GENERATOR 3 DEPOSITS

1.0 INTRODUCTION

On November 3, 1984 a section of tube 40-45 was removed from the tubesheet region of Bruce NGS "A" Unit 3, Steam Generator 3. Samples of the adjacent sludge pile were also obtained. The thickness of the sludge pile at the tube location had been estimated to be 70 mm by eddy current methods; however, during the removal operation the pile height was determined to be 20 mm/1/. The tube sample, approximately 1100 mm long, was cut into several sections as shown in Figure 1/2/.

The integrity of the tube was evaluated by the Metallurgy Department; it was judged to be in excellent condition/2/. The objective of this project was to determine the nature and chemical composition of the tube deposits and sludge samples.

2.0 SAMPLE DESCRIPTION AND EXPERIMENTAL

2.1 Tube Deposits

Visual inspection showed that the outside tube surface was mostly covered with a thin deposit. The surface was inspected with a low magnification optical microscope. A tube section was cut which comprised a small part of the rolled joint, the rolled joint transition, and a region on the secondary side likely to have been under the sludge pile. The deposits on this tube section were examined by Scanning Electron Microscopy with Energy Dispersive X-ray capability (SEM-EDX) and by X-ray Diffraction (XRD). Similar analyses were carried out on a flake of deposit located 50 mm from the rolled joint on the secondary side (ie, above the sludge pile).

2.1 Sludge Pile Deposits

The sludge particles were received in four plastic bottles labelled according to the tool used in the sampling. Each bottle also contained water which had been used in the collection process. Solid and liquid fractions were separated by filtration through a 0.24 µm Millipore filter. The amounts of solid sample and water in each bottle are listed in Table 1.

The total amount of sludge pile deposits was 170 mg. The samples consisted of small chunks (2 to 3 mm in cross-section) and powder. The sample colour was mainly dark brown but some of the biggest chunks showed a bright red coloration. The sludge fractions were analyzed on the filter paper by X-ray fluorescence (XRF). This technique has the same limitations as EDX in that only elements of atomic number greater than that for sodium are satisfactorily detected. Selected chunks were individually examined by SEM-EDX. Crystalline species were identified by XRD. A single composite sludge sample was prepared by mixing the subsamples and was solubilized by fusion with lithium metaborate. The resulting solutions were analyzed by Atomic Absorption Spectroscopy (AAS). The amount of sample was insufficient for any further analyses.

The water fractions which had accompanied the sludge samples were analyzed by AAS for cationic species and by Ion Chromatography (IC) for anionic species.

3.0 RESULTS AND DISCUSSION

3.1 Tube Deposit Evaluation

Figure 2 shows optical micrographs of the tube section corresponding to the rolled joint region taken at 70° intervals. The bottom part of the micrographs corresponds to the rolled joint. This area is characterized by the presence of yellow-brown streaks which in some cases extend well up the tube beyond the rolled joint as shown in Figure 2c. Damage produced by the disintegrator used to relax the tube is shown in Figures 2a, 2b and 2f. The damaged area was arbitrarily assigned the 0° orientation. Figure 2 shows several distinctive zones on the tube surface: (1) The rolled joint region, identified by the rust streaks. (2) A band of grey deposits above the rolled joint, approximately 4 mm wide; this band corresponds to the tube/tubesheet crevice which can nominally vary between 1.6 and 3.2 mm. (3) A zone of thin white deposits which extends up to 20 mm above the grey region. The upper boundary is discontinuous but it can be clearly observed in some areas (Figure 2e). The white deposits likely correspond to the sludge pile which was also estimated at 20 mm at the time of sampling/1/.

No major deposits were observed above the sludge pile zone with the exception of some small flakes (size 3 to 5 mm) of corrosion products. One of these flakes, situated 50 mm above the rolled joint region, was removed and analyzed. The general absence of deposits and the fact that only thin deposits were detected is probably a consequence of the sampling technique. Only thin deposits firmly bound onto the tube surface could have survived the pulling through the tubesheet hole.

3.2 Tube Deposit Analysis

3.2.1 Corrosion Product Flake

The size of the corrosion product flake was approximately 4 by 5 mm and 0.1 to 0.3 mm thick. It had a convex and a concave surface. Table 2 lists several EDX area scans which covered most of the surface of the flake. The main constituents are iron, copper, zinc and nickel. These elements account for 90% of detected elements (ie, those with atomic numbers greater than 11). Minor constituents include chromium, manganese, aluminum and silicon. No sulphur or chlorine was detected. The composition of the concave and convex surfaces is similar although the zinc and silicon concentrations are slightly higher on the convex side. The average composition of the flake as measured by EDX is comparable to that of other free-surface tube deposits from Unit 4, Steam Generator 3 examined previously/3/.

The crystalline phases identified by XRD are shown in Table 3. Major species are magnetite and copper. Possible minor species are cuprite (Cu_2O) and calcium sulphate. These results are consistent with the elemental composition determined by EDX with the exception of calcium sulphate. Despite the tentative XRD identification, it is unlikely that this species is present in significant concentration because of the absence of calcium and sulphur in the EDX spectra.

3.2.2 Rolled Joint/Sludge Pile Tube Deposits

A coupon which included the different deposit zones described in Section 3.1 was cut from the rolled joint region. Its dimensions were 30 mm long by 5 mm wide. Figure 3 shows the region from which the coupon was cut. The orientation was 180° from the disintegration line. Examination by SEM showed a fairly rough rolled joint surface with superficial mechanical deformations probably caused during removal. The crevice region surface was covered with a compact deposit. A micrograph of the interface between these two regions is shown in Figure 4.

Elemental analysis of the coupon surface deposits by EDX is shown in Table 4. The spectra of the rolled joint region are characterized by a strong interference from the tube metal, resulting in high concentrations of nickel and chromium. In addition to these elements, iron is the only major constituent; the remaining elements detected are in concentrations less than 3%. Visual inspection revealed a red deposit in the form of streaks on the rolled region. This deposit is likely to be rust, ie, oxide-hydroxides such as lepidocrocite (FeO(OH)) and goethite (FeO(OH)); and haematite. The oxide-hydroxides do not form under reducing steam generator conditions while they form readily at room temperature in a humid atmosphere such as that during sampling. The rust streaks were likely caused by the tube pulling through the tubesheet during removal. Traces of tubesheet carbon steel may have been imbedded in the tube and were later oxidized to rust in the atmosphere.

The main elemental constituent of the tubesheet crevice deposits is iron which amounted to more than half the weight of the elements detected. Nickel and chromium contributions are significant but may be partially a result of interference by the underlying metal since the deposits were thin. Other important constituents are silicon and aluminum. The remaining elements are present in less than 3% concentrations. The average composition of the crevice deposits is similar to that of deposits from the tube/support plate broached hole crevices of a Unit 4 steam generator examined earlier (see Table 5/3/). This

similarity suggests that the tubesheet crevice deposits are mainly the result of particulate deposition and hideout precipitation reactions and are not locally grown magnetite from corrosion of the tubesheet carbon steel. However, this does not entirely preclude the possible existence of linearly grown magnetite in the tubesheet crevice, particularly since this type of corrosion would likely start only after the crevice was filled with deposits. Detailed inspection of the tubesheet hole bore during future tube removals could provide more direct information on the extent (if any) of tubesheet corrosion.

Figure 5 shows an area of the tube deposits in the sludge region. The location of several EDX point analyses is indicated and the results are shown in Table 6. These results reveal high concentrations of silicon, manganese, magnesium and calcium which apparently follow parallel trends. This indicates that these elements likely form a compound, probably a complex silicate. Feedtrain material constituents, namely iron, copper, zinc, nickel and chromium are also significant but the iron concentration is lower than in the tubesheet crevice deposits. Chlorine and potassium are also present in these analyses and were similarly present in the more general area scans presented in Table 4. The presence of these elements is a result of hideout and they are likely to be accompanied by sodium although the latter element could not be satisfactorily detected by the EDX instrument used. The presence of detectable amounts of these species in the deposits indicates that higher concentrations were originally present since these salts are readily soluble in water. Sulphur was also detected and is likely to be present in the form of sulphate. The existence of this species was confirmed in a previous analysis of Bruce steam generator U-bend deposits/3/.

The crystalline phases in the sludge pile tube deposits were determined in-situ by XRD. The results are shown in Table 7. The tubesheet crevice deposits and the sludge pile deposits were measured separately. In these analyses, the major phase identified was elemental nickel. The deposits were very thin and metal lattice interference was unavoidable. Magnetite was identified in each region as a minor constituent. Elemental copper was identified in the sludge pile region as a minor constituent while its identification was only tentative in the crevice region. The crystalline phases detected are consistent with the elemental composition detected by EDX; however, no silicon compounds could be identified despite the significant concentration of silicon measured in the sludge deposits. Larger amounts of sample may be necessary for a satisfactory XRD analysis.

3.3 Water Analysis

Table 8 shows the analyses of the water fractions of the tubesheet sludge pile samples. The pH was seven in most of the samples with the exception of Chip 1 which showed a pH of 6.2. Therefore there was an increase in the pH in three samples with respect to that of deionized water which is typically less than seven. This increase in pH is a result of the species present in the water samples which likely originated in the sludge. More information on the acid/base forming tendency of the steam generator deposits could be obtained by monitoring the steam generator water during shutdown.

The specific conductivity of the samples was generally high compared to that of steam generator water and it correlated with the total ionic concentrations in each sample. Chloride and sulphate concentrations were significant, 31 mg/ℓ for chloride and 84 mg/ℓ for sulphate in sample Cutter 4 which had the highest

conductivity. Sodium and potassium were present in similar concentrations. This is somewhat surprising since the concentration of sodium in Lake Huron water is much higher than that of potassium (four to five times approximately). Also, water samples from Pickering sludge piles had a sodium to potassium ratio similar to that of Lake Ontario water/4/. The higher potassium contribution in the samples may be related to the water treatment plant at Bruce and/or to the nature of feedwater in-leaked species. Chloride and (sodium plus potassium) are present in approximately stoichiometric concentrations. Similarly, combined calcium and magnesium concentrations are approximately equimolar with sulphate. Fluoride and nitrate concentrations are below the detectability limit in most samples but measurable in the Cutter 4 sample.

It is likely that the ionic species in the water samples leached out of the sludge sample during transportation from the station to the laboratory. The contribution of these species to the sludge pile composition can then be calculated from the volume of water in the sample, the species concentration and the mass of the corresponding sludge sample. The result of this calculation shows that the contributions of sodium and potassium chlorides may be between 1 and 10% of the sludge. However, these results should be viewed with caution. Contamination of the water samples with sodium and potassium chloride from the sludge pile leachate during sample collection will greatly influence the results particularly when the mass of solid sludge is small.

3.4 Sludge Analysis

3.4.1 X-Ray Fluorescence

The Millipore filter papers with the solid sludge samples after filtration were analyzed by XRF. The elements detected and their relative peak heights with respect to the iron peak are shown in Table 9. Iron and copper were major constituents and the remaining elements detected were mainly the same as were found by EDX in the tube deposits. These elements include zinc, nickel, chromium, manganese, silicon, calcium and sulphur; aluminum and potassium were only measured in trace amounts. Exceptions to this were magnesium and chlorine which were not detected in the filters but were detected in the tube deposits.

3.4.2 X-Ray Diffraction

Table 10 shows the crystalline phases identified by XRD in the sludge samples. The major constituents in all the samples were magnetite and metallic copper. Cuprite (Cu_2O) was also a major constituent in the Chip 1 and Chip 2 samples and a minor species in Cutter 4. In the latter sample, lepidocrocite was also identified as a major constituent and goethite as a minor. While magnetite, copper and cuprite have been identified as the main constituents of U-bend deposits in CANDU steam generators/3-6/, iron oxide-hydroxides have not been previously identified. These compounds have a relatively low thermal stability and dehydrate to α-Fe_2O_3 (haematite) at 55°C/7/. Magnetic iron-rich particles were identified in the Cutter 4 sample deposits and were separated from the remainder. These particles may be filings from the tubesheet steel produced during sampling. Since the sludge samples were kept in oxygenated water for several days before filtration, the iron oxide-hydroxides may have formed during this period from the oxidation of the steel particles. To verify this hypothesis, carbon steel filings were degreased and stored in 3 mℓ of Cutter 4 filtrate. After three days a red surface growth could already be observed. The

suspension was filtered after six days and the solid fraction analyzed by XRD. The species identified were magnetite, lepidocrocite and metallic iron.

3.4.3 SEM-EDX Analysis

Three small sludge chunks were analyzed by SEM-EDX. Figure 6 shows the microcrystalline structure of these chunks. The prevalent crystal shape formed a coral-like growth as shown in Figure 7. The chemical composition of these crystals was determined by EDX and the results are listed in Table 11 as analyses 1 and 2. The major elemental constituents were iron and copper which were present in similar concentrations. A trace of sulphur was detected in one analysis. Another type of microcrystal present in the sludge particles has an acicular form. A cluster of these crystals can be seen in the center of Figure 8. The elemental compositions of the cluster and of a randomly chosen individual crystal correspond to analyses 3 and 4, respectively, in Table 11. Iron is the predominant constituent (approximately 80% of the detected elements). Copper is also important (16 to 18%). Silicon and sulphur are detected but in low concentrations.

An interesting feature of some regions of these sludge particles is the presence of large crystals which seem to be bound to the adjacent crystals by microcrystalline growths (as shown in Figure 9). The elemental composition of these crystals (Analysis 5, Table 11) is similar to that of the needle-like microcrystals. Iron and copper are the only significant elemental constituents and silicon and sulphur are measured in low concentrations.

The largest particle is the sludge sample Cutter 4 is shown in Figures 10(a) and (b) which correspond to the top and bottom view of the particle, respectively. The particle was covered on one side (Figure 10a) with a bright red growth. The elemental composition determined by EDX correspond to Analyses 6, 7 and 8 in Table 11. Iron accounts for approximately 90% of all detected elements; copper, manganese, calcium and sulphur constituted the remainder. The colour of the particle, the X-ray diffraction results and its elemental composition confirms that the particle is covered with iron oxide-hydroxides. The core of the particle consisted of carbon steel. Another particle of the same Cutter 4 sample showed a featureless surface in which only iron could be detected (Analyses 9, 10 and 11, Table 11) in significant concentrations. This area also corresponded to a carbon steel surface.

3.4.4 Bulk Chemical Analysis

The three sludge samples were mixed together and the largest chunks were manually separated and put aside. The elemental composition of the remainder of the sample as determined by bulk chemical analysis is shown in Table 12. Iron is the most abundant element, the second in importance is copper. Silicon, calcium and magnesium, as well as nickel and zinc are present in concentrations greater than 10 g/kg. Other elements detected and measured in lower concentrations include chromium, aluminum, manganese and sodium. Tin, potassium and titanium, which had been identified in previous deposit analyses, could not be detected. Because of sample size limitations total sulphur and carbon were not determined.

The analysis shows that the sample has the same elemental constituents as were previously identified and measured in U-bend steam generator deposits from Bruce NGS "A"/3,5,6/.

3.4.5 Sludge Pile Chemistry and Impact on Materials

The main constituents of the sludge sample are: magnetite; metallic copper; cuprous oxide; silicates, sulphates and oxides of calcium, magnesium, aluminum, and possibly manganese. Zinc may be present as a silicate (it was identified in this form in previous deposit analyses/5/) or as an oxide. Chromium and nickel are likely to be present either as single metal oxides or combined spinels with iron. It is possible that significant concentrations of alkaline metal chlorides exist in the sludge pile.

In view of the small size of the sludge samples examined, it is difficult to draw firm conclusions on the quantitative composition of the entire sludge pile since the small sample size makes any result necessarily very local. In addition, this small sample size makes the results susceptible to interference by the presence of very small quantities of contaminants. For instance, the presence of steel filings may erroneously lead to the conclusion that high concentrations of magnetite are present in the samples. Similarly, the concentrations of soluble species in the water samples may have been influenced by contamination with sludge pile leachate.

No porosity values could be obtained from the sludge samples. However, if experience at Pickering may be applicable, a sludge pile porosity between 20 and 35% should be expected. If this porosity range is combined with the potential concentrations of sodium and potassium chlorides and in the sludge as calculated from the water samples, a solution concentration between 3 and 30% may exist under the sludge pile during operation and shutdown.

Laboratory work has shown that the presence of soluble lake water contaminants (sulphate, chlorides) and oxidizing potentials (presence of dissolved oxygen) have a synergistic effect on the corrosion of Bruce steam generator materials beneath simulated sludge piles and under operating conditions/8/. Thus the presence of high concentrations of contaminants may not be detrimental to the structural materials as long as the oxidizing potential is low. This potential is a function of factors such as the pH and the presence of oxidants such as dissolved oxygen or copper oxides. A shift in the oxidation potential of the medium may cause corrosion rates to become unacceptably high for continued satisfactory steam generator reliability. The removal of the sludge piles would minimize the impact of such an occurrence.

4.0 CONCLUSIONS

1. The composition of free tube deposits near the tubesheet is similar to that of U-bend deposits in Bruce NGS "A" steam generators.

2. Deposits in the tubesheet/rolled joint crevice are likely to be mainly the result of particulate deposition and/or hideout precipitation rather than locally grown magnetite from corrosion of the tubesheet carbon steel.

3. The height of the tubesheet sludge pile near the tube was approximately 20 mm. Sludge pile deposits contain important concentrations of species with relatively high solubility such as silicates, sulphates and chlorides of alkaline and alkaline-earth metals. The remainder of the sludge pile consisted of magnetite, metallic copper and cuprous oxide.

4. The composition of the sludge deposits, the species found in the water samples and the probable physical characteristics of the sludge pile indicate that high concentrations of sodium and potassium chlorides may exist under the pile during operation and shutdown.

5. High contaminant concentrations under the pile may not be necessarily detrimental to the structural materials if the oxidation potential of the system is low. However, a shift in this potential may cause unacceptable corrosion. The removal of the sludge pile would minimize the impact of such an event.

5.0 RECOMMENDATIONS

1. Detailed inspection of the tubesheet bore in future tube samplings may provide information on the possible formation of magnetite in the crevice at the secondary face.

2. It is necessary to obtain larger sludge samples from several tubesheet regions for a better understanding of the sludge pile chemical composition and physical characteristics.

3. Monitoring of steam generator water during shutdown may provide information on the nature of hideout species in the steam generator sludge pile. It is important that the monitoring start as soon as possible after the steaming stops.

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TABLE 1

Sludge Mass and Water Volume in Each Sample
From Bruce NGS, Unit 3, Steam Generator 3

Sample Label	Water Volume (mℓ)	Sludge Mass (g)
CHIP-1	51	0.006
CHIP-2	35	0.036
CUTTER-3	69	<0.001
CUTTER-4	55	0.128

TABLE 2

EDX Analysis of Corrosion Product Flake

Region	Analysis	Sample Area mm^2	Elemental Weight % of Detected Species							
			Fe	Cu	Zn	Ni	Cr	Mn	Si	Al
Concave	1	2.8	42	33	16	6.4	0.4	0.7	0.5	1.6
	2	2.8	43	33	15	6.1	0.3	0.5	0.5	1.6
	3	2.8	39	39	14	5.3	0.1	0.4	0.6	1.5
Convex	4	108	47	24	22	4.6	0.4	0.5	0.7	1.2
	5	1.0	44	23	26	4.2	0.1	0.5	1.1	1.3
	6	2.8	38	33	21	3.7	0.2	0.9	1.9	1.4
Mean			42	31	19	5.1	0.25	0.58	0.88	1.4
			3.3	6.1	4.7	1.1	0.13	0.18	0.55	0.16

TABLE 3

Crystalline Phases in Corrosion Product Flake
Determined by X-Ray Diffraction

Major: Magnetite, Copper

Possible Minor: Cuprite (Cu_2O), Calcium Sulphate

TABLE 4

EDX Analysis of Corrosion Products on Coupon
From Tubesheet Region of Bruce Unit 3 Steam Generator 3

Region	Analysis	Sample Area mm^2	Fe	Cu	Zn	Ni	Cr	Mn	Si	Al	Ca	Mg	S	Cl	K
Rolled Joint	1	0.25	52	2.9	2.4	27	10	2	1.3	0.7	1.1	0.2	1.2	-	-
	2	0.11	19	1.9	2.0	58	14	1	1.1	0.6	1.0	0.2	1.0	-	-
		Mean	36	2.4	2.2	43	12	1.5	1.2	0.7	1.0	0.2	1.1	-	-
Crevice	3	0.25	63	2.2	2.0	7.3	2.7	2.3	9.9	4.6	2.3	2.9	0.7	-	-
	4	0.01	57	2.0	1.8	9.5	3.5	2.6	12	6.4	1.2	3.8	0.4	-	-
	5	0.25	61	1.8	1.3	9.7	4.4	1.6	10	7.3	0.5	1.5	0.4	-	-
	6	0.11	46	1.6	1.9	29	13	1.7	2.8	1.4	1.4	0.3	1.1	-	-
	7	4.0	57	1.8	2.5	17	9	2.1	5.2	2.8	1.3	0.3	1.1	0.9	-
	8	4.0	50	1.7	1.6	23	11	1.9	4.6	2.6	1.4	0.7	1.0	0.9	-
	9	7E-3	59	2.5	2.5	12	5.8	2.4	8.4	4.7	1.2	0.5	1.0	0.8	0.9
	10	2E-4	67	2.6	1.6	5.7	2.6	2.4	8.1	5.6	1.0	0.5	1.0	0.9	1.0
		Mean	58	2.0	1.9	14	6.5	2.1	7.6	4.4	1.3	1.3	0.8	0.4	0.2
		Std Dev.	7	0.4	0.4	8	4	0.4	3.1	2.0	0.5	1.3	0.3	0.5	0.4
Sludge Pile	11	0.25	10	4.3	9.5	13	4.5	12	32	-	4.6	8.5	0.5	-	-
	12	0.25	6.6	2.8	7.0	4.8	1.0	16	47	-	2.9	11	0.3	-	-
	13	7E-3	5.0	1.0	8.7	3.4	0.7	15	48	-	3.6	14	0.5	-	-
	14	0.25	10	1.6	4.3	9.9	4.1	11	33	-	22	2.3	0.6	-	-
	15	0.25	14	3.9	4.5	7.9	3.1	6.3	31	0.8	26	2.3	0.5	-	-
	16	2E-3	8.0	1.6	4.4	6.4	2.8	16	33	0.1	24	2.2	0.6	0.2	1.1
	17	2E-3	11	2.2	6.0	9.6	5.4	11	28	0.5	23	1.7	0.7	0.4	1.1
	18	0.25	17	3.6	7.1	30	11	6	18	-	2.2	4.5	0.2	-	-
	19	4.0	33	4.3	4.8	21	7.5	3.8	13	2.0	8.3	2.2	0.6	0.1	-
	20	4.0	35	3.9	4.9	18	6.6	4.2	13	2.1	8.6	2.3	0.6	0.1	0.5
	21	1.0	24	6.7	8.2	14	5.5	7.1	17	1.4	14	1.6	0.4	0.2	0.7
		Mean	16	3.3	6.3	13	4.7	9.9	28	0.62	13	4.8	0.5	0.1	0.3
		Std Dev.	10	1.6	1.9	7.9	3.0	4.6	12	0.83	9	4.3	0.2	0.1	0.5

TABLE 5

EDX Analyses of Tube Deposits at the 7th Support and Scallop Bar/Tube Intersections, Unit 4, Steam Generator 3 (from Reference 3, Tables 5 and 6)

Region		Elemental Weight % of Detected Species										
		Fe	Cu	Zn	Ni	Al	Mn	Cr	Si	Ca	Mg	S
Crevice (Table 5)	Mean	59	8	10	8.9	0.6	2.9	2.0	7.3	0.9	0.5	1.4
	Std Dev.	9	5	5	12	0.7	1.2	3.9	3.8	1.0	1.0	0.7
Flow (Table 5)	Mean	28	45	5.6	17	-	0.5	3.1	-	-	-	-
	Std Dev.	7	21	1.9	10	-	0.6	7.0	-	-	-	-
Free Surface (Table 6)	Mean	53	21	11	13	-	-	0.8	-	-	-	-
	Std Dev.	3.6	4.2	2.2	2.9	-	-	0.9	-	-	-	-

TABLE 6

EDX Point Analyses of Sludge Region Tube Deposits

Analysis*	Elemental Weight % of Detected Species												
	Fe	Cu	Zn	Ni	Cr	Mn	Si	Al	Ca	Mg	S	Cl	K
1	52	1.8	2.2	4.1	2.4	7.3	14	0.4	11	1.0	1.9	1.2	0.7
2	15	2.3	7.5	4.4	16	18	29	0.2	19	1.8	0.5	0.2	0.9
3	4.3	1.4	3.9	3.7	1.6	21	37	-	24	2.6	0.5	0.1	1.0
4	3.6	6.4	3.7	3.6	1.7	20	34	0.2	23	2.1	0.5	0.4	1.0

* Analysis locations are shown in Figure 5.

TABLE 7

Crystalline Phases in Tube Deposits
Determined by X-Ray Diffraction

Region	Phases
Crevice	Major: Nickel Minor: Magnetite Possible Minor: Copper
Sludge	Major: Nickel Minor: Magnetite, Copper

TABLE 8

Analyses of Water Samples

Sample	pH	Conductivity mS/m	Ionic Species concentration, mg/ℓ							
			Cl^-	SO_4^{2-}	F^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
Chip-1	6.2	80	14	9.3	<0.2	<0.5	4.2	0.14	6.2	4.4
Chip-2	7.0	228	33	39	<0.2	<0.5	18	0.28	16	14
Cutter-3	7.0	158	8.8	46	0.4	<0.5	20	1.1	5.0	6.0
Cutter-4	7.1	320	31	84	1.1	2.6	33	2.2	15	19

TABLE 9

Analysis of Sludge Samples from Bruce Unit 3
Steam Generator 3 by X-Ray Fluorescence

Sample	Spectral Peak Height, % of Iron Peak										
	Fe	Cu	Zn	Ni	Cr	Mn	Si	Al	Ca	S	K
Chip-1	100	43	10	5.1	2.5	3.7	2.9	t	2.7	4.3	t
Chip-2	100	61	8	3.0	1.5	2.8	4.8	t	0.9	1.1	t
Cutter-3	t	t	-	-	-	-	t	-	-	t	t
Cutter-4	100	15	3.9	1.2	2.1	4.9	1.6	t	2.6	0.7	-

t: trace
-: not detected

TABLE 10

Crystalline Phases Identified by X-Ray Diffraction
in Sludge Deposits from Bruce Unit 3, Steam Generator 3

Sample	Magnetite Fe_3O_4	Metallic Copper Cu^o	Cuprite Cu_2O	Lepidocrocite FeO(OH)	Goethite FeO(OH)	Calcite $CaCO_3$
Chip-1	M	M	M	-	-	-
Chip-2	M	M	M	-	-	-
Cutter-4*	M	M	m	M	m	pm

M: Major

m: minor

pm: possible minor

* Sample Cutter-4 contained magnetic metal fragments, likely steel.

TABLE 11

EDX Analyses of Sludge Pile Particles

Analysis	Elemental Weight % of Detected Species							
	Fe	Cu	Ni	Mn	Si	Ca	S	Area (mm^2)
1	52	48	-	-	-	-	-	1.1E-3
2	50	50	-	-	-	-	0.2	Point
3	80	18	-	-	0.5	-	1.1	1.0E-4
4	83	16	-	-	0.3	-	1.4	Point
5	87	11	-	-	1.0	-	0.4	Point
6	97	1.4	-	-	1.8	-	0.2	1.0E-3
7	85	7.4	-	3.3	2.4	1.8	0.3	0.25
8	88	4.6	-	3.7	1.9	1.6	0.2	0.25
9	96	1.7	-	1.7	0.5	-	0.2	Point
10	95	2.6	-	0.1	1.8	-	0.1	Point
11	95	3.4	-	0.1	0.9	-	0.2	Point

TABLE 12

Bruce NGS, Unit 3, Steam Generator 3
Sludge Pile Deposits. Elemental Concentrations, (g/kg)

	Fe	Cu	Zn	Ni	Cr	Mn	Si	Al	Ca	Mg	Na	Sn	K	Ti	Sum of Detected Elements
Elemental Conc.	370	130	23	11	5	0.64	50	6.3	18	14	0.14	<2	<0.13	<5	628

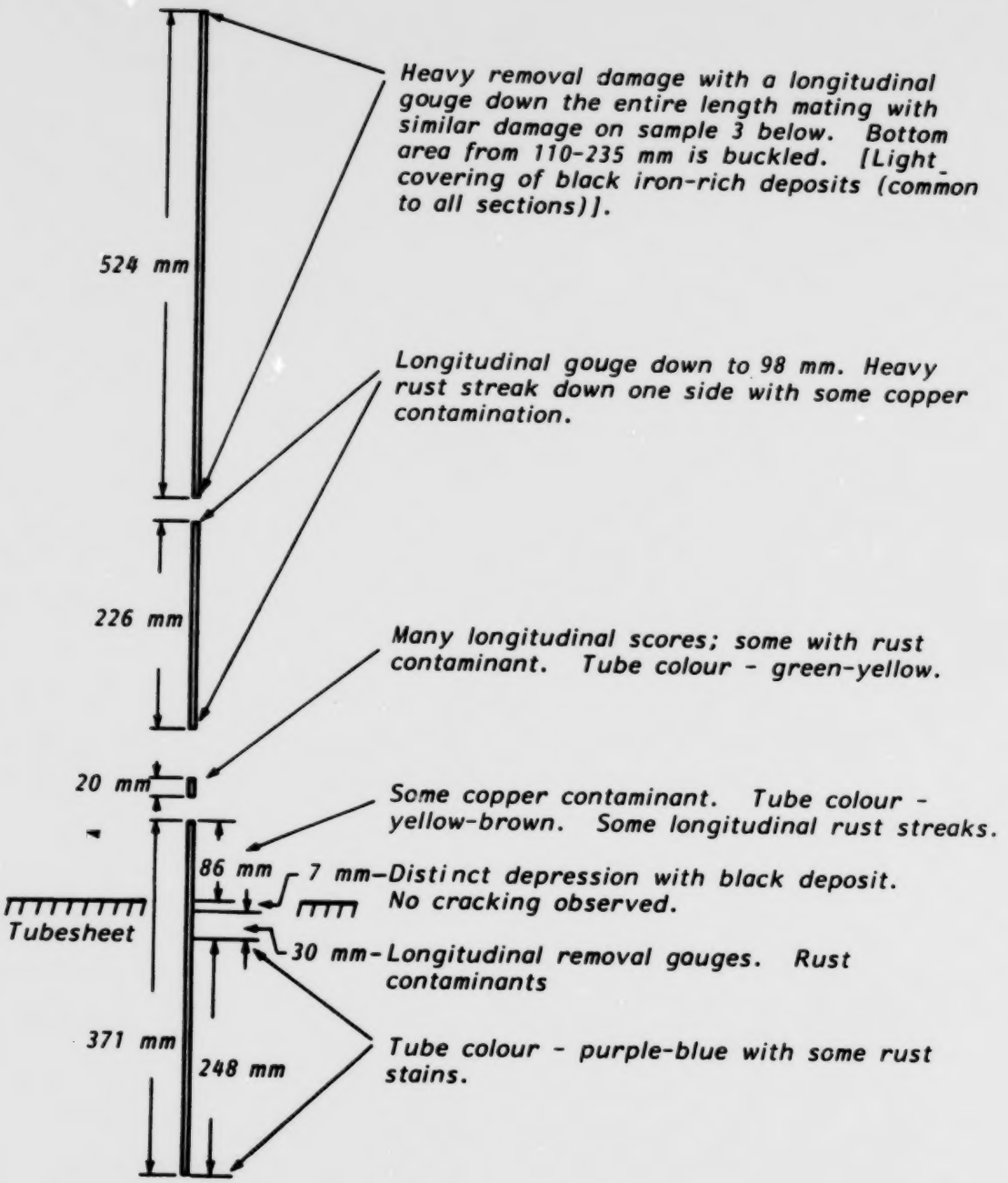
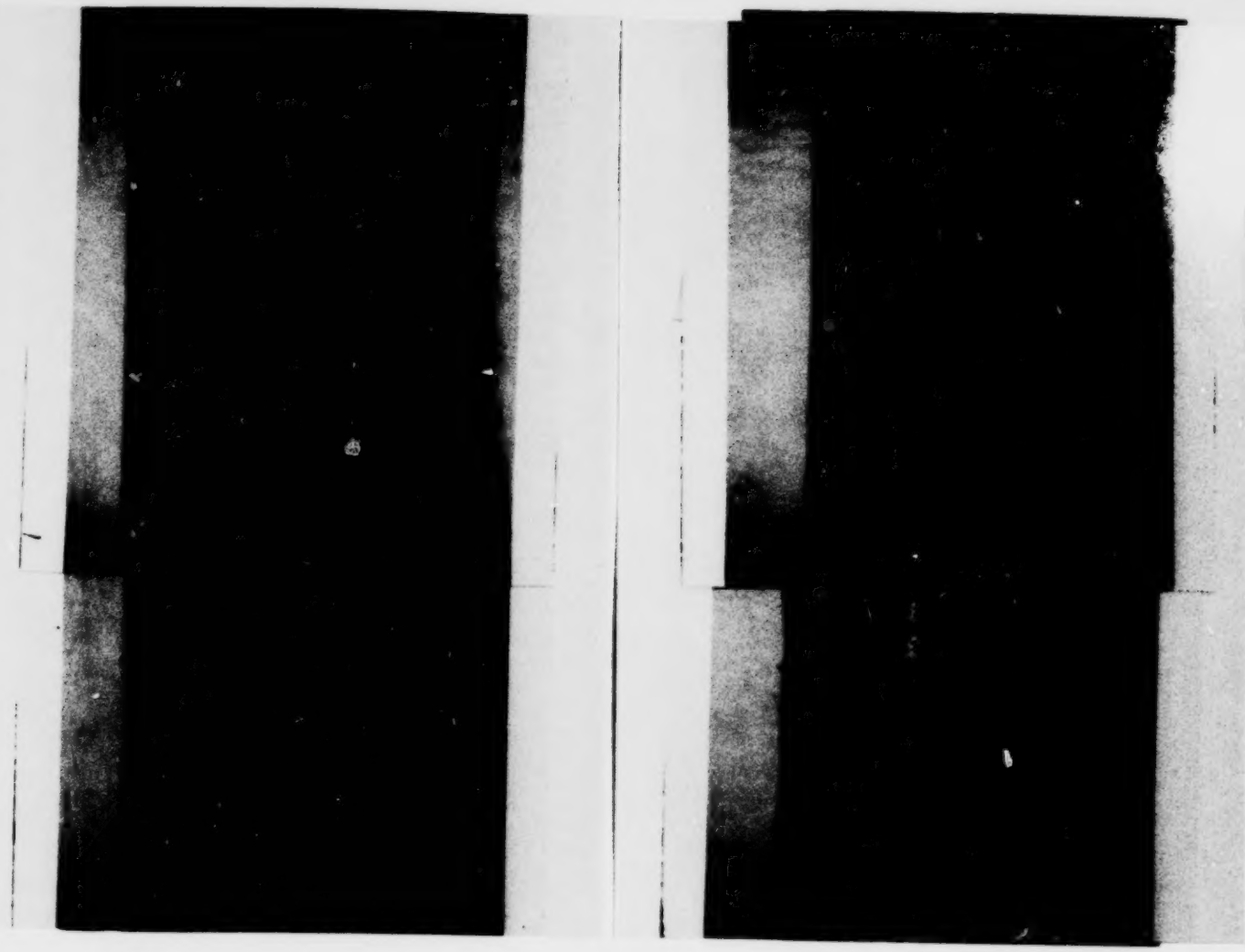

524 mm
226 mm
20 mm
86 mm
7 mm
Tubesheet
30 mm
371 mm
248 mm
Heavy removal damage with a longitudinal gouge down the entire length mating with similar damage on sample 3 below. Bottom area from 110-235 mm is buckled. [Light covering of black iron-rich deposits (common to all sections)].
Longitudinal gouge down to 98 mm. Heavy rust streak down one side with some copper contamination.
Many longitudinal scores; some with rust contaminant. Tube colour - green-yellow.
Some copper contaminant. Tube colour - yellow-brown. Some longitudinal rust streaks.
Distinct depression with black deposit. No cracking observed.
Longitudinal removal gouges. Rust contaminants
Tube colour - purple-blue with some rust stains.

FIGURE 1 (Reference 2)

SUBMITTED TUBE SAMPLES AND THEIR DISPOSITION WITHIN THE STEAM GENERATOR

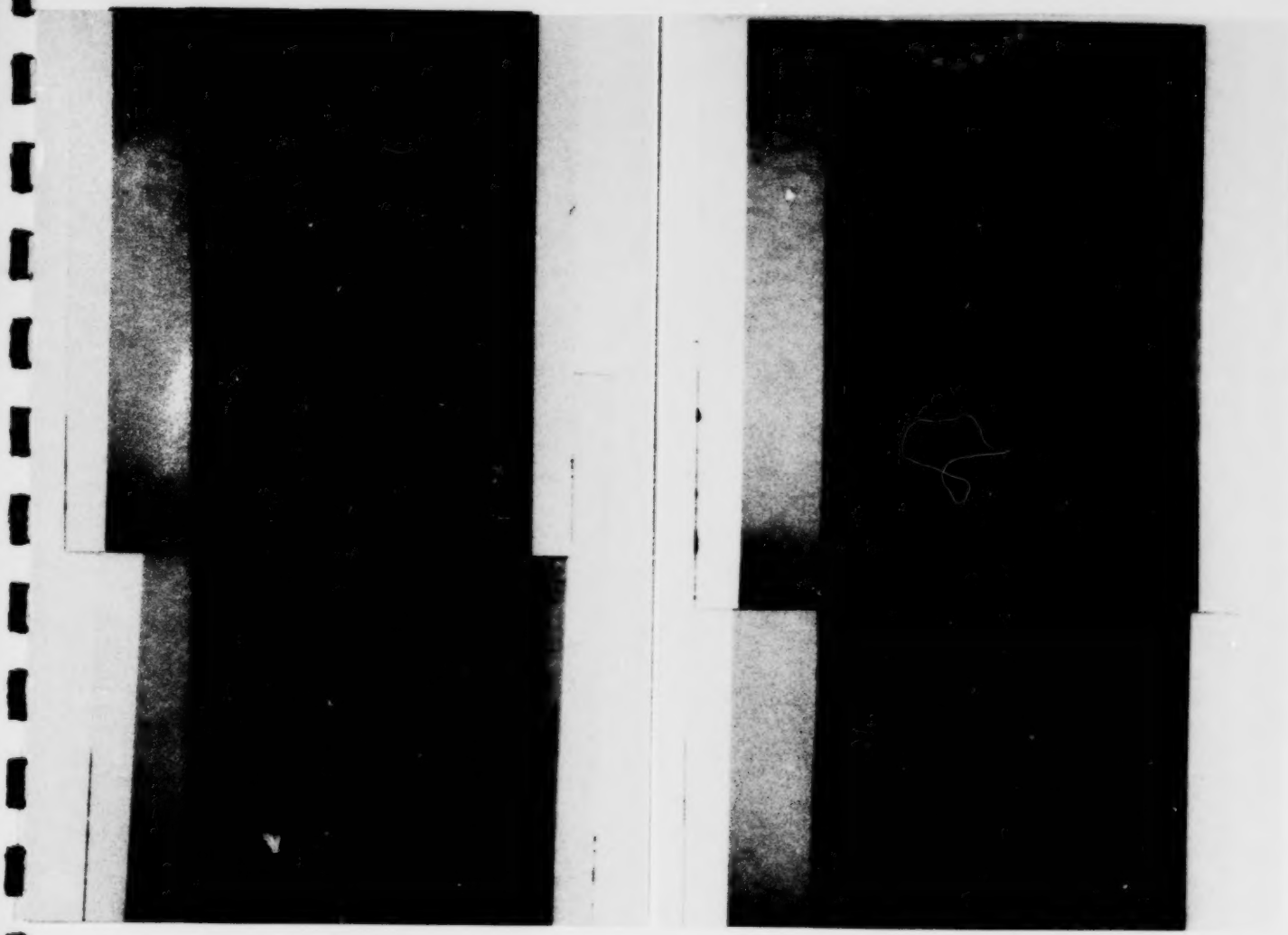


(a) Orientation 0°

(b) Orientation 70°

FIGURE 2

TUBE 40-45 BRUCE NGS 'A' UNIT 3 STEAM GENERATOR 3 REGION
AT THE TUBESHEET ROLLED JOINT
0° ORIENTATION IS ASSIGNED TO THE DISINTEGRATION LINE

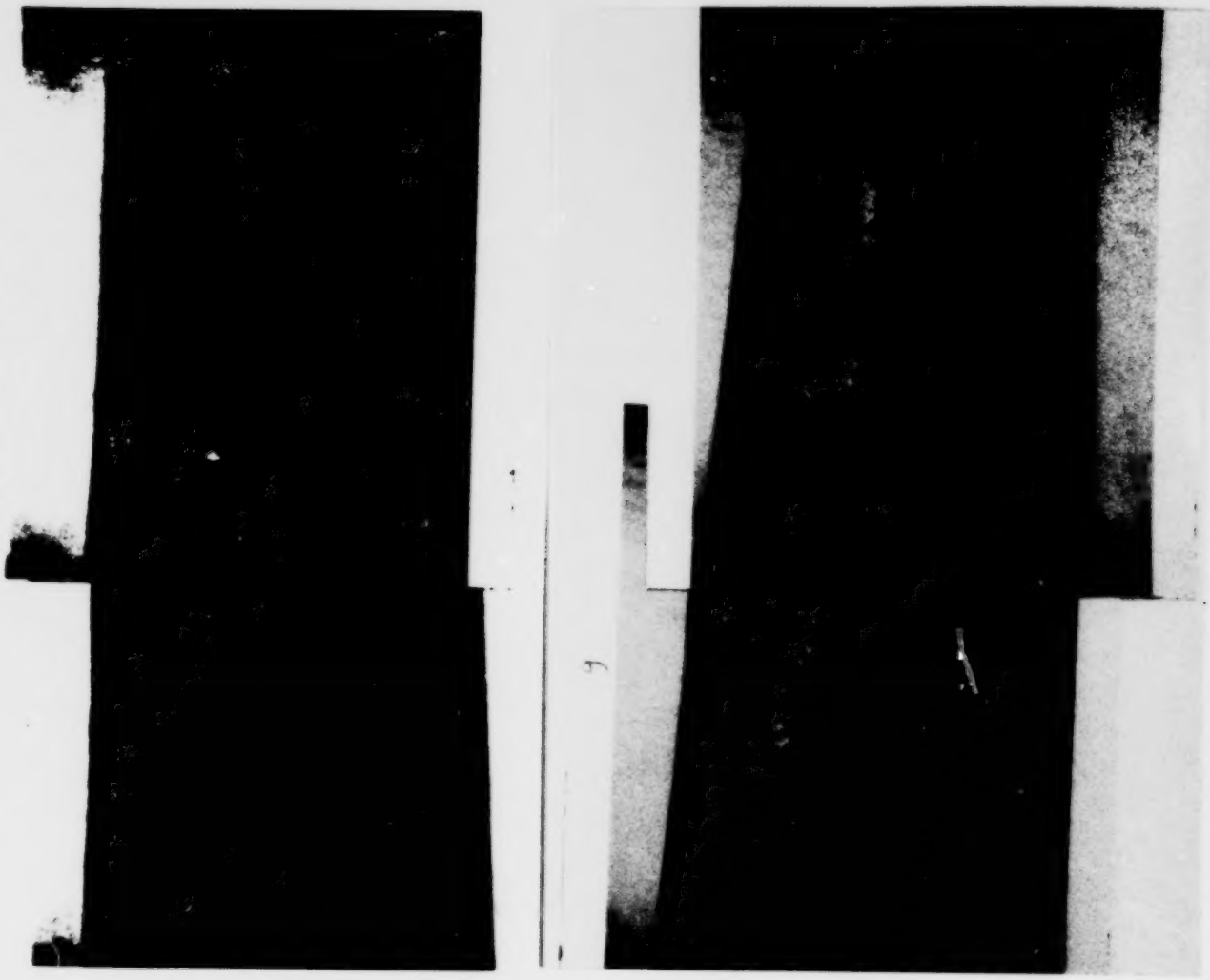


(c) Orientation 140°

(d) Orientation 210°

FIGURE 2

TUBE 40-45 BRUCE NGS 'A' UNIT 3 STEAM GENERATOR 3 REGION
AT THE TUBESHEET ROLLED JOINT
0° ORIENTATION IS ASSIGNED TO THE DISINTEGRATION LINE



(e) Orientation 280°

(f) Orientation 350°

FIGURE 2

TUBE 40-45 BRUCE NGS 'A' UNIT 3 STEAM GENERATOR 3 REGION
AT THE TUBESHEET ROLLED JOINT.
0° ORIENTATION IS ASSIGNED TO THE DISINTEGRATION LINE

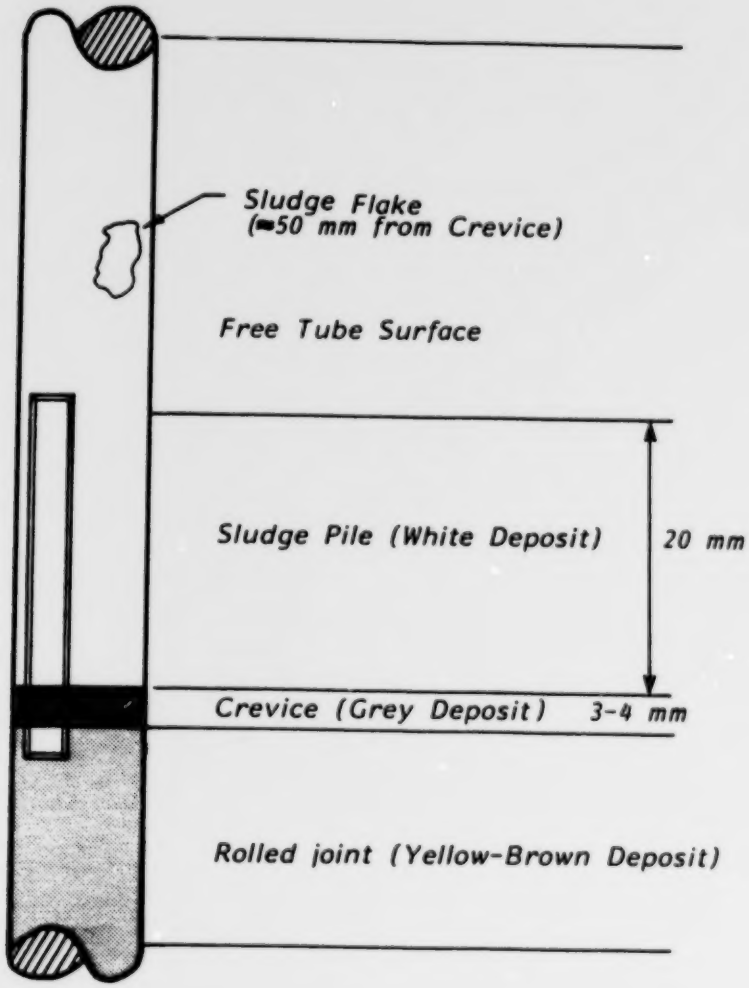


FIGURE 3

**REGIONS IN BRUCE NGS 'A"
UNIT 3, STEAM GENERATOR 3 TUBE SAMPLE AT THE TUBE/TUBESHEET INTERSECTION. THE POSITION OF THE SAMPLE TUBE COUPON IS INDICATED. THE ORIENTATION WAS 180° FROM THE DISINTEGRATION LINE**

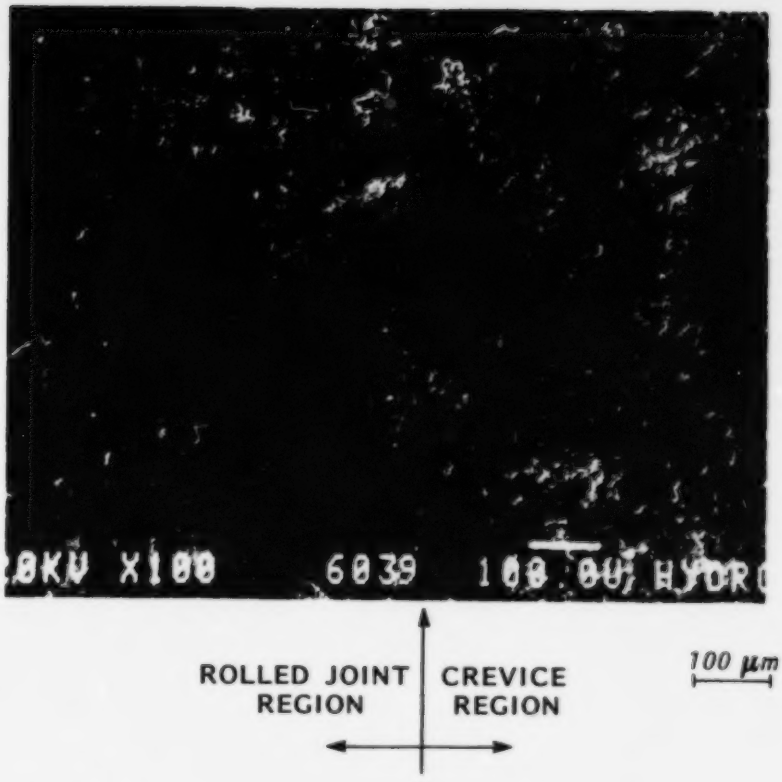


FIGURE 4

BRUCE TUBE COUPON, UNIT 3, STEAM GENERATOR 3. INTERFACE BETWEEN THE ROLLED JOINT REGION AND THE CREVICE REGION. THE LATTER IS COVERED WITH DEPOSITS

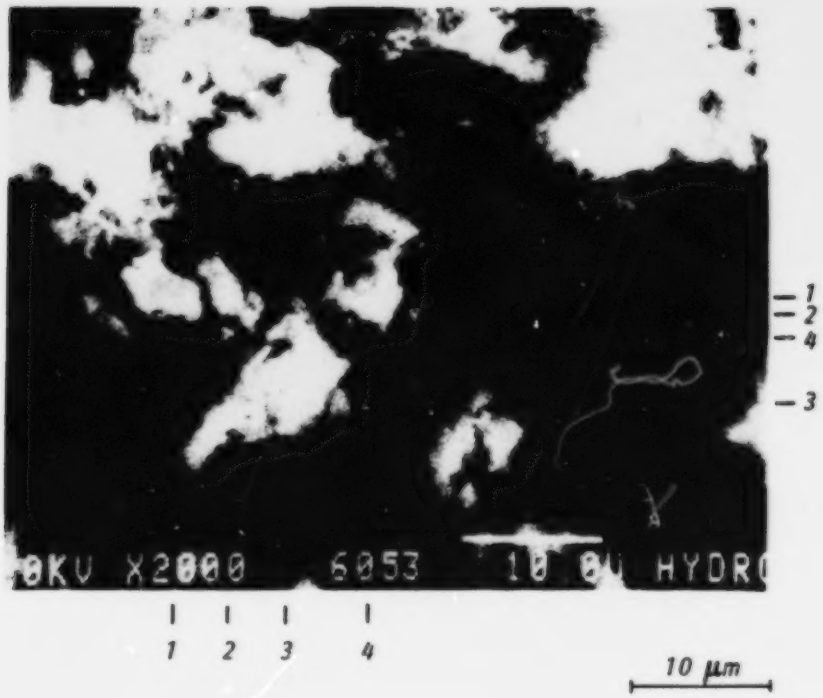


FIGURE 5

TUBE DEPOSITS IN SLUDGE REGION. NUMBERS INDICATE EDX POINT ANALYSIS LOCATIONS. RESULTS ARE IN TABLE 6

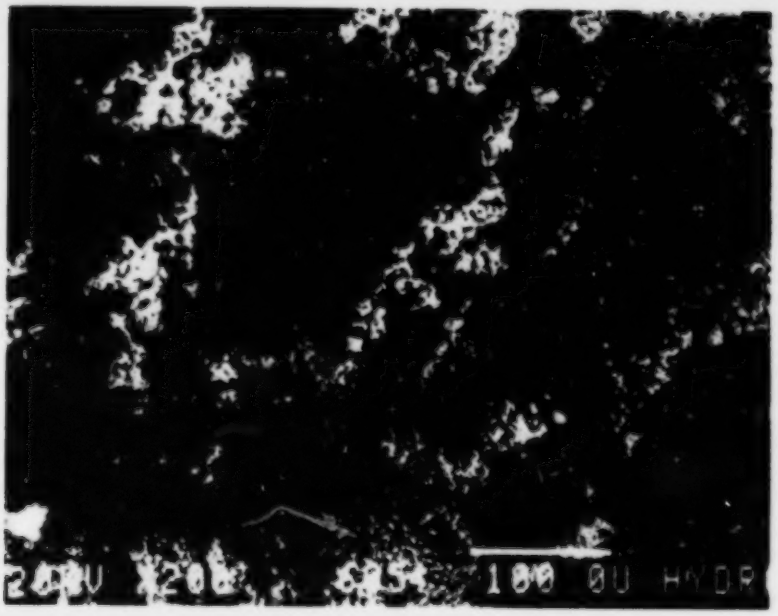


FIGURE 6

SLUDGE SAMPLE CUTTER 4. THE MICROGRAPH SHOWS THE TWO TYPES OF CRYSTALS

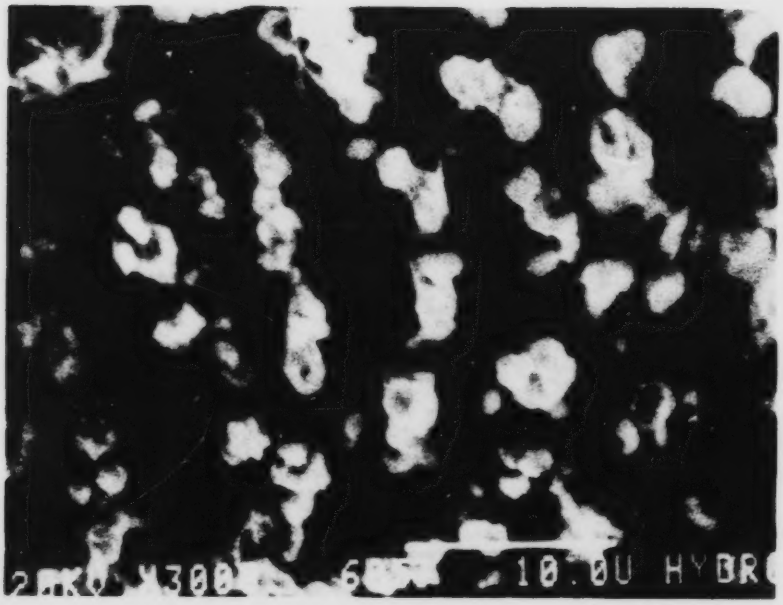


FIGURE 7

SLUDGE SAMPLE CUTTER 4. MICROCRYSTALS FORMING A CORAL-LIKE STRUCTURE

FIGURE 8

SLUDGE SAMPLE CUTTER 4. ROUND MICROCRYSTALS FORM A CORAL-LIKE STRUCTURE. NEEDLE-LIKE CRYSTALS IN THE CENTRE FORM A CROSS-LINKED LATTICE

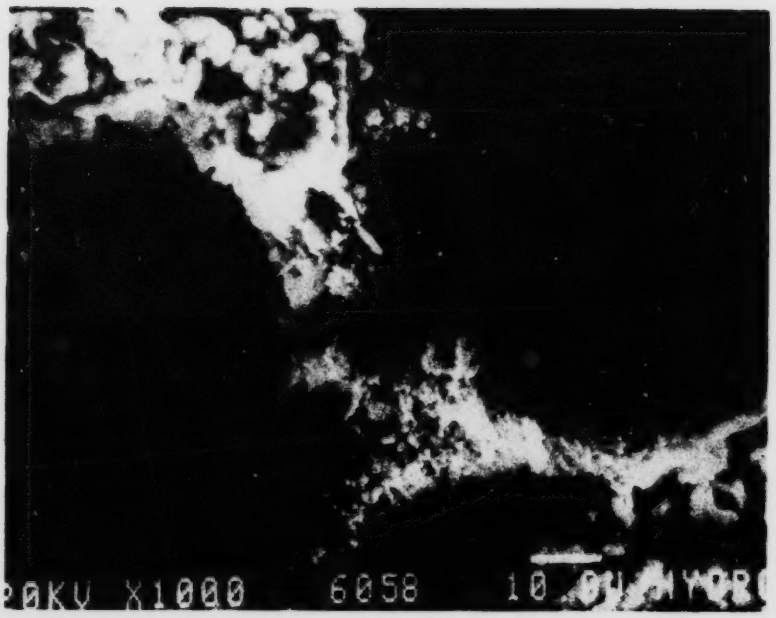


FIGURE 9

DETAIL OF A SLUDGE PARTICLE WHICH SHOWS A LARGE PARTICLE ON THE RIGHT ATTACHED TO THE ADJACENT SURFACE BY A CRYSTALLINE GROWTH

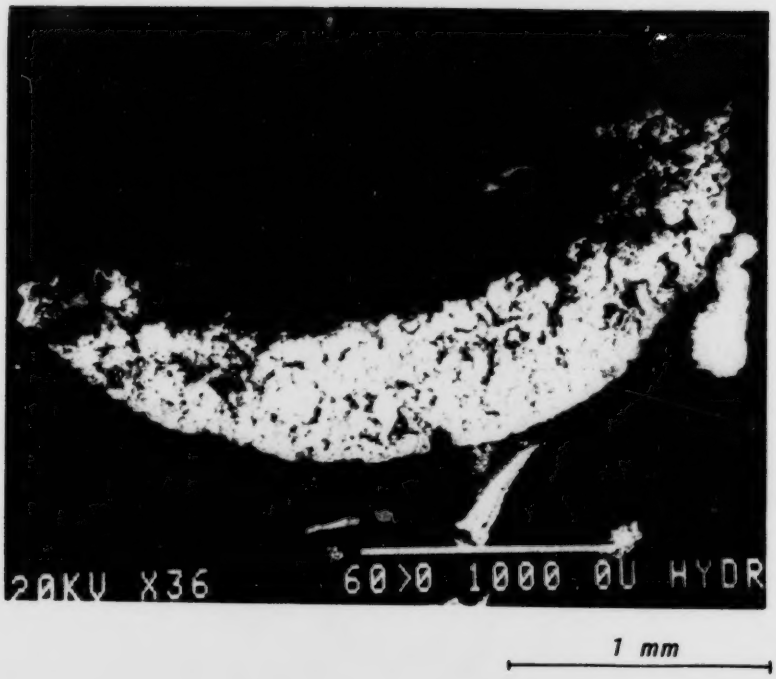


FIGURE 10a

TOP VIEW OF THE LARGEST PARTICLE IN SAMPLE CUTTER 4
THE SURFACE WAS COVERED WITH A BRIGHT RED GROWTH

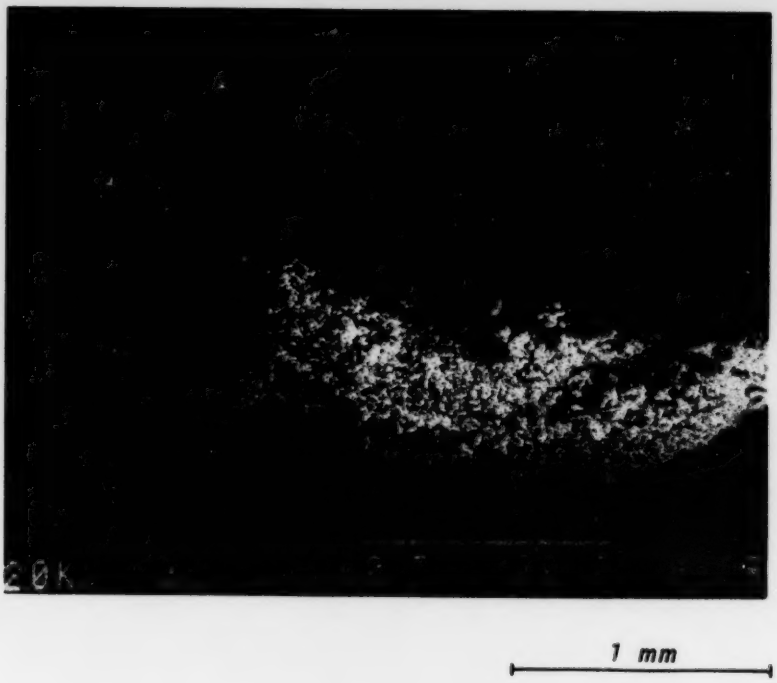


FIGURE 10b

BOTTOM VIEW OF THE LARGEST PARTICLE IN SAMPLE CUTTER 4

100 µm

FIGURE 11

PARTICLE IN SLUDGE SAMPLE CUTTER 4 FLAT SURFACE
IN THE CENTRE CORRESPOND TO CARBON STEEL